

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,

COMPRISING A DIAMINOPYRAZOLE OR A TRIAMINOPYRAZOLE AND

A HALOGENATED META-AMINOPHENOL, AND DYEING PROCESS

5

The present invention relates to a composition for the oxidation dyeing of keratin fibres, in particular human keratin fibres such as the hair, comprising at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles, in combination 10 with at least one meta-aminophenol which is halogenated ortho to the phenol, as coupler, and to the dyeing process using this composition with an oxidizing agent.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions 15 containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols or heterocyclic compounds such as pyrazole derivatives, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation 20 bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by means of a process of oxidative condensation.

It is also known that the shades obtained 25 with oxidation bases can be varied by combining them with suitably selected couplers or coloration

modifiers, the latter possibly being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

5 The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy 10 a certain number of requirements. Thus, it must have no toxicological drawbacks, it must allow shades to be obtained in the desired intensity and it must satisfactorily withstand external agents (light, bad weather, washing, permanent-waving, perspiration or 15 rubbing).

The dyes must also be able to cover white hair, and, lastly, they must be as unselective as possible, i.e. they must allow only the smallest possible differences in colour along the same keratin 20 fibre, which may in fact be differently sensitized (i.e. damaged) between its tip and its root.

Compositions for the oxidation dyeing of keratin fibres, containing pyrazole derivatives such as 4,5-diaminopyrazoles, 3,4-diaminopyrazoles or 3,4,5-triaminopyrazoles as oxidation base, in combination 25 with couplers conventionally used for oxidation dyeing,

such as, for example, meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers such as, for example, indole derivatives, have already been proposed, in particular in German patent

- 5 applications DE 3 843 892, DE 4 234 887, DE 4 234 886, DE 4 234 885 and DE 195 43 988. However, such compositions are not entirely satisfactory, in particular as regards the fastness of the colorations obtained with regard to the various attacking factors
10 to which the hair may be subjected, and in particular with regard to perspiration.

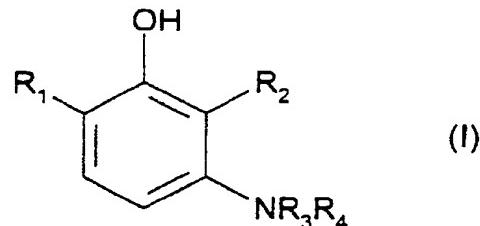
However, the Applicant has now discovered that it is possible to obtain novel powerful dyes that are particularly resistant to the various attacking factors to which the hair may be subjected, by combining, as oxidation base, at least one diaminopyrazole and/or at least one triaminopyrazole and, as coupler, a meta-aminophenol halogenated in a position ortho to the phenol.
15

- 20 This discovery forms the basis of the present invention.

A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibres and in particular human keratin fibres such as the
25 hair, characterized in that it comprises, in a medium which is suitable for dyeing:

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- at least one oxidation base chosen from diaminopyrazoles and triaminopyrazoles;
 - and at least one coupler chosen from the halogenated meta-aminophenols of formula (I) below, and the
- 5 addition salts thereof with an acid:



in which:

- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a halogen atom such as 10 chlorine, bromine, iodine or fluorine, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkoxy radical or a C₂-C₄ polyhydroxyalkoxy radical;
- R₃ and R₄, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical or a C₁-C₄ monoaminoalkyl radical; it being understood that at least one of the radicals R₁ 20 and R₂ represents a halogen atom.

The oxidation dye composition in accordance with the invention makes it possible to obtain intense colorations in varied shades, which are relatively

unselective and which have excellent properties of resistance both with respect to atmospheric agents such as light and bad weather, and with respect to perspiration and the various treatments to which the

5 hair may be subjected (shampooing, permanent-waving).

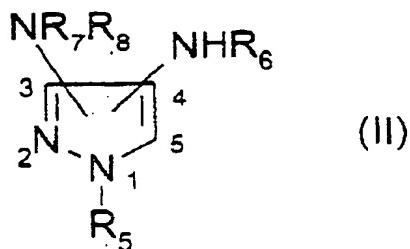
These properties are particularly noteworthy especially as regards the resistance of the colorations with respect to perspiration.

Among the C₁-C₄ alkyl and C₁-C₄ alkoxy radicals
10 of the compounds of formula (I) above, mention may be made in particular of the methyl, ethyl, propyl, methoxy and ethoxy radicals.

Among the halogenated meta-aminophenols of formula (I), mention may be made more particularly of
15 3-amino-6-chlorophenol, 3-amino-6-bromophenol, 3-(β-aminoethyl)amino-6-chlorophenol, 3-(β-hydroxyethyl)-amino-6-chlorophenol and 3-amino-2-chloro-6-methylphenol, and the addition salts thereof with an acid.

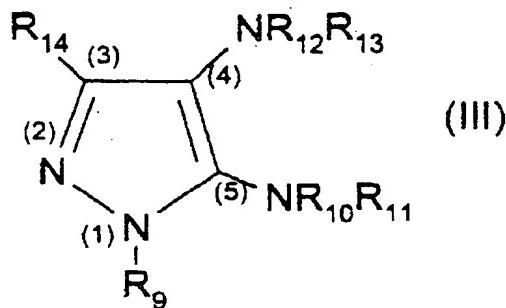
20 Among the diaminopyrazoles which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of:

a) the diaminopyrazoles of formula (II) below, and the
25 addition salts thereof with an acid:



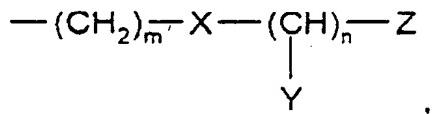
in which:

- R₅ represents a hydrogen atom, a C₁-C₆ alkyl radical, a C₂-C₄ hydroxyalkyl radical, a benzyl radical, a phenyl radical, a benzyl radical substituted with a halogen atom or with a C₁-C₄ alkyl or C₁-C₄ alkoxy group, or forms, with the nitrogen atom of the group NR₇R₈ in position 5, a hexahydropyridazine or tetrahydropyrazole heterocycle which is optionally monosubstituted with a C₁-C₄ alkyl group;
- R₆ and R₇, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, a C₂-C₄ hydroxyalkyl radical, a benzyl radical or a phenyl radical;
- R₈ represents a hydrogen atom, or a C₁-C₆ alkyl or C₂-C₄ hydroxyalkyl radical; with the proviso that R₆ represents a hydrogen atom when R₅ represents a substituted benzyl radical or forms a heterocycle with the nitrogen atom of the group NR₇R₈ in position 5;
- b) the diaminopyrazoles of formula (III) below, and the addition salts thereof with an acid:



in which:

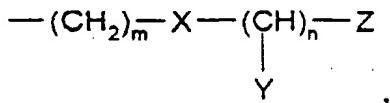
- R_9 , R_{10} , R_{11} , R_{12} and R_{13} , which may be identical or different, represent a hydrogen atom; a linear or branched C_1-C_6 alkyl radical; a C_2-C_4 hydroxyalkyl radical; a C_2-C_4 aminoalkyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or a C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro, trifluoromethyl, amino or C_1-C_4 alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C_1-C_4 alkyl, C_1-C_4 alkoxy, methylenedioxy or amino radical; or a radical



- in which m and n are integers, which may be identical or different, between 1 and 3 inclusive, X represents an oxygen atom or an NH group, Y represents a hydrogen atom or a methyl radical, and Z represents a methyl radical, a group OR or NRR' in which R and R' , which may be identical or different, denote a hydrogen atom, a methyl radical or an ethyl radical,

it being understood that when R_{10} represents a hydrogen atom, then R_{11} can also represent an amino or C_1-C_4 alkylamino radical,

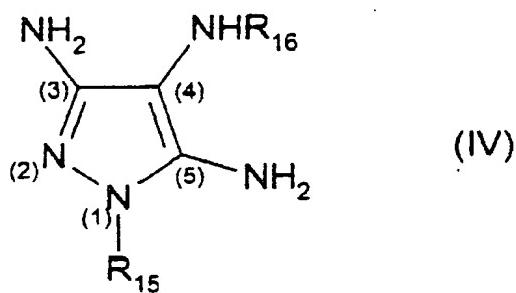
- R_{14} represents a linear or branched C_1-C_6 alkyl radical; a C_1-C_4 hydroxyalkyl radical; a C_1-C_4 aminoalkyl radical; a (C_1-C_4) alkylamino(C_1-C_4)alkyl radical; a di(C_1-C_4) alkylamino(C_1-C_4)alkyl radical; a hydroxy(C_1-C_4) alkylamino(C_1-C_4)alkyl radical; a (C_1-C_4) alkoxyethyl radical; a phenyl radical; a phenyl radical substituted with a halogen atom or with a C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro, trifluoromethyl, amino or C_1-C_4 alkylamino radical; a benzyl radical; a benzyl radical substituted with a halogen atom or with a C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro, trifluoromethyl, amino or C_1-C_4 alkylamino radical; a heterocycle chosen from thiophene, furan and pyridine, or alternatively a radical $-(CH_2)_p-O-(CH_2)_q-OR''$, in which p and q are integers, which may be identical or different, between 1 and 3 inclusive, and R'' represents a hydrogen atom or a methyl radical,
- it being understood that, in formula (III) above,
 - at least one of the radicals R_{10} , R_{11} , R_{12} and R_{13} represents a hydrogen atom,
 - when R_{10} , or R_{12} , respectively, represents a substituted or unsubstituted phenyl radical, or a benzyl radical or a radical



then R_{11} , or R_{13} , respectively, cannot represent any of these three radicals,

- 5 - when R_{12} and R_{13} simultaneously represent a hydrogen atom, then R_9 can form, with R_{10} and R_{11} , a hexahydropyrimidine or tetrahydroimidazole heterocycle which is optionally substituted with a $\text{C}_1\text{-}\text{C}_4$ alkyl or 1,2,4-tetrazole radical,
- 10 - when R_{10} , R_{11} , R_{12} and R_{13} represent a hydrogen atom or a $\text{C}_1\text{-}\text{C}_6$ alkyl radical, then R_9 or R_{14} can also represent a 2-, 3- or 4-pyridyl, 2- or 3-thienyl or 2- or 3-furyl heterocyclic residue which is optionally substituted with a methyl radical or alternatively a cyclohexyl radical.

Among the triaminopyrazoles which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds of formula (IV) below, and the addition salts thereof with an acid:



in which:

- R_{15} and R_{16} , which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_2-C_4
- 5 hydroxyalkyl radical.

Among the diaminopyrazoles of formula (II) above, mention may be made more particularly of 4,5-diamino-1-(4'-methoxybenzyl)pyrazole, 4,5-diamino-1-(4'-methylbenzyl)pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1-(3'-methoxybenzyl)pyrazole, 4-amino-1-(4'-methoxybenzyl)-5-methylaminopyrazole, 4-amino-5-(β -hydroxyethyl)amino-1-(4'-methoxybenzyl)pyrazole, 4-amino-5-(β -hydroxyethyl)amino-1-methylpyrazole, 4-amino-(3)5-methylaminopyrazole, 3-(5)4-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-benzylpyrazole, 3-amino-4,5,7,8-tetrahydropyrazolo[1,5-a]pyrimidine, 7-amino-2,3-dihydro-1H-imidazolo[1,2-b]pyrazole and 3-amino-8-methyl-4,5,7,8-tetrahydropyrazolo[1;5-a]pyrimidine, and the addition salts thereof with an acid.

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The diaminopyrazoles of formula (III) are known compounds which can be prepared according to the synthetic process as described, for example, in French patent application FR-A-2 733 749.

- 5 Among the diaminopyrazoles of formula (III) above, mention may be made more particularly of:
- 1-benzyl-4,5-diamino-3-methylpyrazole,
 - 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methoxyphenyl)-pyrazole,
 - 10 - 4,5-diamino-1-(β -hydroxyethyl)-3-(4'-methylphenyl)-pyrazole,
 - 4,5-diamino-1-(β -hydroxyethyl)-3-(3'-methylphenyl)-pyrazole,
 - 4,5-diamino-3-methyl-1-isopropylpyrazole,
 - 15 - 4,5-diamino-3-(4'-methoxyphenyl)-1-isopropylpyrazole,
 - 4,5-diamino-1-ethyl-3-methylpyrazole,
 - 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
 - 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
 - 20 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-tert-butylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-phenylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-(2'-methoxyphenyl)-pyrazole,
 - 25 - 4,5-diamino-3-hydroxymethyl-1-(3'-methoxyphenyl)-pyrazole,

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- 4,5-diamino-3-hydroxymethyl-1-(4'-methoxyphenyl)-pyrazole,
- 1-benzyl-4,5-diamino-3-hydroxymethylpyrazole,
- 4,5-diamino-3-methyl-1-(2'-methoxyphenyl)pyrazole,
- 5 - 4,5-diamino-3-methyl-1-(3'-methoxyphenyl)pyrazole,
- 4,5-diamino-3-methyl-1-(4'-methoxyphenyl)pyrazole,
- 3-aminomethyl-4,5-diamino-1-methylpyrazole,
- 3-aminomethyl-4,5-diamino-1-ethylpyrazole,
- 3-aminomethyl-4,5-diamino-1-isopropylpyrazole,
- 10 - 3-aminomethyl-4,5-diamino-1-tert-butylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-ethylpyrazole,
- 4,5-diamino-3-dimethylaminomethyl-1-isopropyl-
- pyrazole,
- 15 - 4,5-diamino-3-dimethylaminomethyl-1-tert-butyl-
- pyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-ethylpyrazole,
- 4,5-diamino-3-ethylaminomethyl-1-isopropylpyrazole,
- 20 - 4,5-diamino-3-ethylaminomethyl-1-tert-butylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-methylpyrazole,
- 4,5-diamino-3-methylaminomethyl-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-methylaminomethylpyrazole,
- 1-tert-butyl-4,5-diamino-3-methylaminomethylpyrazole,
- 25 - 4,5-diamino-3-[(β -hydroxyethyl)aminomethyl]-1-methyl-
- pyrazole,

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- 4,5-diamino-3-[$(\beta$ -hydroxyethyl)aminomethyl]-1-isopropylpyrazole,
- 4,5-diamino-1-ethyl-3-[$(\beta$ -hydroxyethyl)aminomethyl]-pyrazole,
- 5 - 1-tert-butyl-4,5-diamino-3-[$(\beta$ -hydroxyethyl)aminomethyl]pyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1,3-dimethylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-isopropyl-3-methyl-pyrazole,
- 10 - 4-amino-5-(β -hydroxyethyl)amino-1-ethyl-3-methyl-pyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-tert-butyl-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-phenyl-3-methyl-15 pyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-(2-methoxyphenyl)-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-(3-methoxyphenyl)-3-methylpyrazole,
- 20 - 4-amino-5-(β -hydroxyethyl)amino-1-(4-methoxyphenyl)-3-methylpyrazole,
- 4-amino-5-(β -hydroxyethyl)amino-1-benzyl-3-methyl-pyrazole,
- 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,

- 4-amino-1-tert-butyl-3-methyl-5-methylaminopyrazole,
- 4,5-diamino-1,3-dimethylpyrazole,
- 4,5-diamino-3-tert-butyl-1-methylpyrazole,
- 4,5-diamino-1-tert-butyl-3-methylpyrazole,
5 - 4,5-diamino-1-methyl-3-phenylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
- 4,5-diamino-1-(β -hydroxyethyl)-3-phenylpyrazole,
- 4,5-diamino-1-methyl-3-(2'-chlorophenyl)pyrazole,
- 4,5-diamino-1-methyl-3-(4'-chlorophenyl)pyrazole,
10 - 4,5-diamino-1-methyl-3-(3'-trifluoromethylphenyl)-
pyrazole,
- 4,5-diamino-1,3-diphenylpyrazole,
- 4,5-diamino-3-methyl-1-phenylpyrazole,
- 4-amino-1,3-dimethyl-5-phenylaminopyrazole,
15 - 4-amino-1-ethyl-3-methyl-5-phenylaminopyrazole,
- 4-amino-1,3-dimethyl-5-methylaminopyrazole,
- 4-amino-3-methyl-1-isopropyl-5-methylaminopyrazole,
- 4-amino-3-isobutoxymethyl-1-methyl-5-methylamino-
pyrazole,
20 - 4-amino-3-methoxyethoxymethyl-1-methyl-5-methylamino-
pyrazole,
- 4-amino-3-hydroxymethyl-1-methyl-5-methylamino-
pyrazole,
- 4-amino-1,3-diphenyl-5-phenylaminopyrazole,
25 - 4-amino-3-methyl-5-methylamino-1-phenylpyrazole,

- 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
- 5-amino-3-methyl-4-methylamino-1-phenylpyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-(4'-chlorophenyl)pyrazole,
- 5 - 5-amino-3-ethyl-1-methyl-4-(N,N-methylphenyl)amino-pyrazole,
- 5-amino-1-methyl-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
- 5-amino-3-ethyl-4-(N,N-methylphenyl)aminopyrazole,
- 10 - 5-amino-4-(N,N-methylphenyl)amino-3-phenylpyrazole,
- 5-amino-4-(N,N-methylphenyl)amino-3-(4'-methylphenyl)pyrazole,
- 5-amino-3-(4'-chlorophenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 15 - 5-amino-3-(4'-methoxyphenyl)-4-(N,N-methylphenyl)-aminopyrazole,
- 4-amino-5-methylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-phenylpyrazole,
- 4-amino-5-ethylamino-3-(4'-methylphenyl)pyrazole,
- 20 - 4-amino-3-phenyl-5-propylaminopyrazole,
- 4-amino-5-butylamino-3-phenylpyrazole,
- 4-amino-3-phenyl-5-phenylaminopyrazole,
- 4-amino-5-benzylamino-3-phenylpyrazole,
- 4-amino-5-(4'-chlorophenyl)amino-3-phenylpyrazole,
- 25 - 4-amino-3-(4'-chlorophenyl)-5-phenylaminopyrazole,
- 4-amino-3-(4'-methoxyphenyl)-5-phenylaminopyrazole,

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- 1-(4'-chlorobenzyl)-4,5-diamino-3-methylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
 - 4-amino-1-ethyl-3-methyl-5-methylaminopyrazole,
 - 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

5 and the addition salts thereof with an acid.

Among these diaminopyrazoles of formula (III) above, the ones more particularly preferred are:

- 4,5-diamino-1,3-dimethylpyrazole,
 - 4,5-diamino-3-methyl-1-phenylpyrazole,
 - 10 - 4,5-diamino-1-methyl-3-phenylpyrazole,
 - 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
 - 1-benzyl-4,5-diamino-3-methylpyrazole,
 - 4,5-diamino-3-tert-butyl-1-methylpyrazole,
 - 4,5-diamino-1-tert-butyl-3-methylpyrazole,
 - 15 - 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
 - 4,5-diamino-1-ethyl-3-methylpyrazole,
 - 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
 - 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
 - 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
 - 20 - 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
 - 4,5-diamino-3-methyl-1-isopropylpyrazole,
 - 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

and the addition salts thereof with an acid.

Among the triaminopyrazoles of formula (IV) above, mention may be made more particularly of 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-

diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

The diaminopyrazole(s) and/or the 5 triaminopyrazole(s) in accordance with the invention and/or the corresponding addition salt(s) with an acid preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 6% 10 by weight approximately relative to this weight.

The halogenated meta-aminophenol(s) of formula (I) in accordance with the invention and/or the corresponding addition salt(s) with an acid preferably represent(s) from 0.0001 to 5% by weight approximately 15 relative to the total weight of the dye composition, and even more preferably from 0.005 to 3% by weight approximately relative to this weight.

The dye compositions in accordance with the invention can contain other couplers conventionally 20 used for oxidation dyeing, other than the halogenated meta-aminophenols of formula (I), and/or other oxidation bases conventionally used for oxidation dyeing, other than a diaminopyrazole and a triaminopyrazole and/or direct dyes, in particular in 25 order to modify the shades or to enrich them with glints.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the 5 hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) generally consists of water or of a mixture of water and at least one organic solvent to dissolve the 10 compounds which would not be sufficiently soluble in water. Organic solvents which may be mentioned, for example, are C₁-C₄ lower alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol 15 monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

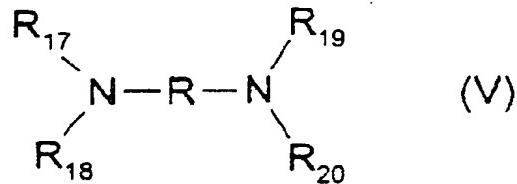
The solvents can be present in proportions 20 preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the dye composition in accordance 25 with the invention is generally between 3 and 12 approximately and even more preferably between 5 and 11

approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres.

Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid and lactic acid, and sulphonic acids.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (V) below:



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in which R is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R₁₇, R₁₈, R₁₉ and R₂₀, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or 20 C₁-C₄ hydroxyalkyl radical.

The dye composition according to the invention can also contain various adjuvants conventionally used in compositions for dyeing the

hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic
5 thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersants, conditioners such as, for example, volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and
10 opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the
15 combination in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The dye composition according to the invention can be in various forms, such as in the form
20 of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

A subject of the invention is also a process for dyeing keratin fibres, and in particular human
25 keratin fibres such as the hair, using the dye composition as defined above.

According to this process, the dye composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing agent which is 5 added to the dye composition just at the time of use, or which is present in an oxidizing composition that is applied simultaneously or sequentially.

According to one particularly preferred embodiment of the dyeing process according to the 10 invention, the dye composition described above is mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The 15 mixture obtained is then applied to the keratin fibres and is left to stand on them for 3 to 60 minutes approximately, preferably 5 to 40 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

20 The oxidizing agent present in the oxidizing composition as defined above can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali 25 metal bromates, persalts such as perborates,

percarbonates and persulphates, and peracids. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such 5 that after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and even more preferably between 5 and 11. It is adjusted to the desired value by means of acidifying or 10 basifying agents usually used in the dyeing of keratin fibres and as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined 15 above.

The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and 20 in particular human hair.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above, 25 and a second compartment of which contains the oxidizing composition as defined above. These devices

can be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

The examples which follow are intended to

5. illustrate the invention without, however, limiting its scope.

EXAMPLES

COMPARATIVE DYEING EXAMPLES 1 TO 4

The dye compositions below, in accordance
10 with the invention, were prepared (contents in grams) :

EXAMPLE	1 (*)	2	3	4
4,5-diamino-1-ethyl-3-methylpyrazole dihydrochloride (oxidation base)	0.639	0.639	0.639	0.639
3-aminophenol (coupler not forming part of the invention)	0.327	-	-	-
3-amino-6-chlorophenol (coupler in accordance with the invention)	-	0.431	-	-
3-(β-aminoethyl)amino-6-chlorophenol (coupler in accordance with the invention)	-	-	0.560	-

EXAMPLE	1 (*)	2	3	4
3 - (β -hydroxyethyl) amino-6-chlorophenol (coupler in accordance with the invention)	-	-	-	0.563
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

(*) : example not forming part of the invention

(**) common dye support:

- Oleyl alcohol polyglycerated with 4.0 g
2 mol of glycerol
- Oleyl alcohol polyglycerated with 5.69 g A.M.
4 mol of glycerol, containing 78% active material (A.M.)
- Oleic acid 3.0 g
- Oleylamine containing 2 mol of 7.0 g
ethylene oxide, sold under the tradename Ethomeen O12® by the company Akzo
- Diethylaminopropyl laurylamino 3.0 g A.M.
succinamate, sodium salt, containing 55% A.M.
- Oleyl alcohol 5.0 g
- Oleic acid diethanolamide 12.0 g
- Propylene glycol 3.5 g
- Ethyl alcohol 7.0 g

- Dipropylene glycol	0.5 g
- Propylene glycol monomethyl ether	9.0 g
- Sodium metabisulphite as an aqueous solution containing 35% A.M.	0.455 g A.M.
- Ammonium acetate	0.8 g
- Antioxidant, sequestering agent	q.s.
- Fragrance, preserving agent	q.s.
- Aqueous ammonia containing 20% NH ₃	10 g

It is important to note that each of the dye compositions 1 to 4 above contains the same molar amount of coupler, i.e. 3×10^{-3} mol.

5 At the time of use, each dye composition above was mixed with an equal amount by weight of an oxidizing composition consisting of a 20-volumes aqueous hydrogen peroxide solution (6% by weight).

10 Each resulting composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

The locks of dyed hair were then subjected to a test of resistance to the action of perspiration.

15 The colour of the locks of hair dyed with compositions 1 to 4 was evaluated in the Munsell system using a Minolta® CM 2002 colorimeter, before the test of resistance to the action of perspiration.

According to the Munsell notation, a colour is defined by the expression H V / C in which the three parameters respectively denote the shade or Hue (H), the intensity or Value (V) and the purity or 5 Chromaticity (C), the oblique line in this expression simply being a convention and not indicating a ratio.

The locks of dyed hair were then subjected to the test of resistance to the action of perspiration.

To do this, the locks of dyed hair were 10 immersed in a crystallizing dish covered with a watch glass and containing a solution of synthetic sweat of the following composition:

- NaCl	1.0 g
- Potassium hydrogen phosphate	0.1 g
15 - Histidine	0.025 g
- Lactic acid qs	pH 3.2
- Distilled water qs	100 g

The locks of dyed hair were left to stand in 20 this synthetic sweat solution for 48 hours at 37°C. The locks were then rinsed, followed by drying.

The colour of the locks was then re-evaluated in the Munsell system using a Minolta® CM 2002 colorimeter.

25 The difference between the colour of the lock before the test of resistance to perspiration and the

colour of the lock after the test of resistance to perspiration was calculated by applying the Nickerson formula

$$\Delta E = 0.4C_0dH + 6dV + 3dC$$

- 5 as described, for example, in "Couleur, Industrie et Technique [Colour, Industry and Technique]"; pages 14-17; vol. No 5; 1978.

In this formula, ΔE represents the difference in colour between two locks, ΔH , ΔV and ΔC represent 10 the variation in absolute value of the parameters H , V and C , and C_0 represents the purity of the lock relative to which it is desired to evaluate the colour difference.

The degradation of the colour is 15 proportionately greater the larger the value of ΔE .

The results are given in the table below:

EXAMPLE	Colour of the hair before the test	Colour of the hair after the test	Degradation of the colour			
			ΔH	ΔV	ΔC	ΔE
1 (*)	9.2 RP 3/3/2.6	2.5 YR 3.9/2.1	13.3	0.6	0.5	18.9
2	2.6 RP 3.0/3.7	6.1 RP 3.5/3.2	3.5	0.5	0.5	9.7
3	2.6 RP 3.0/2.9	4.1 RP 3.0/2.9	1.5	0	0	1.7
4	2.7 RP 3.2/3.2	6.1 RP 3.5/3.0	3.4	0.3	0.2	6.8

These results show that the coloration obtained using the dye composition of Example 1 not forming part of the invention, since it contains a combination of a diaminopyrazole and a non-halogenated meta-aminophenol, is markedly less resistant to the action of perspiration than the colorations obtained using the compositions of Examples 2 to 4, all of which form part of the invention since they contain a combination of a diaminopyrazole and a meta-aminophenol which is halogenated ortho to the phenol.

DYEING EXAMPLES 5 TO 8

The dye compositions below, in accordance with the invention, were prepared (contents in grams) :

EXAMPLE	5	6	7	8
4,5-diaminopyrazole dihydrochloride (oxidation base)	0.513	-	-	-
1-methyl-4,5-diaminopyrazole dihydrochloride (oxidation base)	-	0.555	0.555	0.555
3-amino-2-chloro-6-methylphenol (coupler in accordance with the invention)	0.473	0.473	-	-
3-amino-6-chlorophenol (coupler in accordance with the invention)	-	-	0.431	-
3-(β-aminoethyl)amino-6-chlorophenol (coupler in accordance with the invention)	-	-	-	0.560
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

5 (***) common dye support:

This is identical to the one used for Examples 1 to 4 above.

At the time of use, each dye composition 5 above was mixed with an equal amount by weight of an oxidizing composition consisting of a 20-volumes aqueous hydrogen peroxide solution (6% by weight).

Each resulting composition was applied for 30 minutes to locks of natural grey hair containing 90% 10 white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

The locks were dyed in the shades given in the table below:

EXAMPLE	SHADE OBTAINED
5	Red-coppery
6	Red-coppery
7	Red-iridescent
8	Iridescent red